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Industrial Process Profiles for Environmental Use: Chapter 27 Primary Lead Industry

PEDCo-Environmental, Inc.
Cincinnati, OH

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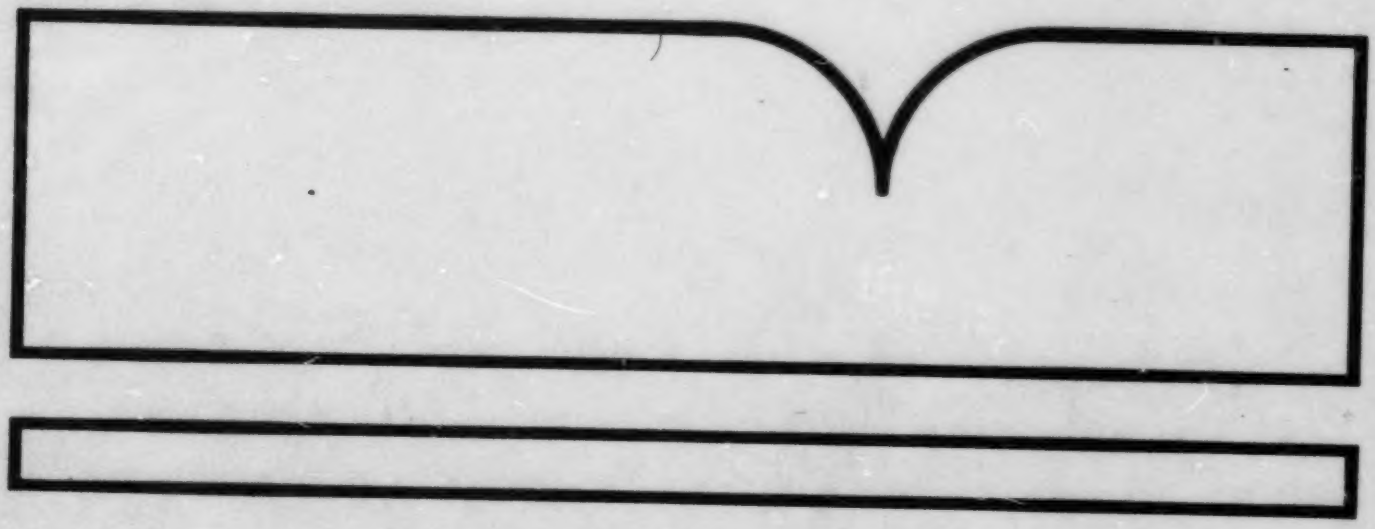

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Chapter 27
Primary Lead Industry

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16. ABSTRACT

The catalog of Industrial Process Profiles for Environmental Use was developed as an aid in defining the environmental impacts of industrial activity in the United States. Entries for each industry are in consistent format and form separate chapters of the study.

The primary lead industry as defined for this study consists of mining, beneficiation, smelting, and refining. A profile of the industry is given including plant locations, capacities, and various statistics regarding production and consumption of lead, co-products, and by-products. The report summarizes the various commercial routes practiced domestically for lead production in a series of process flow diagrams and detailed process descriptions. Each process description includes available data regarding input materials, operating conditions, energy and utility requirements, waste streams produced (air, water, and solid waste), and control technology practices and problems.

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INDUSTRIAL PROCESS PROFILES FOR ENVIRONMENTAL USE: CHAPTER 27 PRIMARY LEAD INDUSTRY

by

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LEAD INDUSTRY

INDUSTRY DESCRIPTION

Although primary lead refinery production increased somewhat in 1978, mine production and consumption declined. Curtailed use of lead antiknock compounds in gasoline accounts for a significant portion of this reduction in spite of the fact that such use still represents 15 percent of lead consumption (1). Other areas of lead consumption have also decreased. Lead pigments are now rarely used in paints, and lead has been partially replaced in such applications as plumbing, battery manufacture, packaging, protective coatings, and construction.

Although new methods of production are being developed, few technological changes have occurred in domestic commercial operations; lead is still being produced with the same pyrometallurgical techniques introduced 75 years ago. The one major exception to this lack of innovation is the replacement of all downdraft sinter machines with the updraft type.

The most significant recent development in the U.S. lead industry was the discovery and development of the "New Lead Belt" in southeastern Missouri. Mining of this deposit began in 1967 and now more than 80 percent of the ore mined in the United States specifically for lead comes from this region. A portion of this deposit consists of almost pure galena, analyzing at over 70 percent lead with only very small amounts of other metals.

Three of the six U.S. lead smelters are near the New Missouri lead belt; the others are located in Idaho, Montana, and Texas. The industry employs about 7000 people; two-thirds of this number are employed in mining and concentrating operations (1).

Raw Materials

Lead is most often found in nature as galena (PbS), the primary sulfide of lead. Deposits are rarely pure since the lead-bearing compound is usually mixed with pyrite, sphalerite, and pyrrhotite. Most of these deposits contain very little copper.

Oxidized lead ores also occur and are composed primarily of anglesite and cerussite, the weathered products of galena. Table 1 lists the important lead ore minerals, together with others in which the lead is combined with phosphorus, vanadium, and other elements.

TABLE 1. LEAD MINERALS, BY NAME AND COMPOSITION

Mineral	Composition	Lead, %
Galena	PbS	88.6
Anglesite	$PbSO_4$	68.3
Cerussite	$PbCO_3$	77.5
Pyromorphite	$Pb_5Cl(PO_4)_3$	76.3
Vanadinite	$Pb_5Cl(VO_4)_3$	73.0
Crocoite	$PbCrO_4$	63.9
Wulfenite	$PbMoO_4$	56.4
Linarite	$PbO \cdot CuO \cdot SO_3\ H_2O$	

Domestic production of lead comes chiefly from ores mined primarily for their lead content. Additional lead is derived from ores in which lead and zinc are comparably valued as coproducts and it is also recovered as a byproduct from ores mined for copper, gold, silver, zinc, or fluorine. Complex ores mined in the Rocky Mountains are greatly dependent for economical recovery on the values of the lead, zinc, silver, and gold content and not the value of just one metal (2). Table 2 list the 25 leading lead producing mines in the United States in 1976.

Most lead produced in this country is from domestic ores. Little is produced from imported concentrates. General imports of lead represented 20 percent of total consumption in 1978 (3). A considerable quantity is produced first at zinc smelters, the residues then being sent to lead smelters for recovery of lead.

In the production of lead metal, the industry requires various other raw materials. Explosives, water, and various organic chemicals are used in mining and concentrating operations; pyrometallurgical smelting and refining require various fluxing materials such as limestone and silica and fuel in the form of coke, oil, or natural gas.

Energy requirements for lead production involving mining, concentrating, smelting, and refining are lower than any of the other major metals. The production of 1 ton of lead is estimated to require 6.8×10^6 kilocalories; this figure is about one-fourth that for refined copper and less than one-half that of zinc (2).

Products

Lead bullion more than 99.9 percent pure is the primary product of this industry. Antimonial lead, a less ductile metal, is also produced. In 1976, the processing of lead ores and concentrates accounted for 100 percent of domestic bismuth production, as well as 56 percent of antimony, and sizable quantities of zinc, silver, tellurium, copper, and gold. Appreciable quantities of sulfur and sulfuric acid are also recovered as byproducts of lead production. Byproduct and coproduct associations in lead production in the rest of the world are similar to those found domestically (2).

Table 3 provides basic 1978 statistics of the lead industry.

Companies

The United States leads the world in lead production, accounting for about 15 percent of the total world mine production in 1978 (3). In that year, the domestic mining industry was comprised of about 35 mines in 11 states with production valued at $398 million (3). The seven leading mines, all in Missouri, produced 88 percent of the year's total mine production of recoverable metal (1).

Domestic primary smelters are located in Missouri, Montana, Texas, and Idaho. As shown in Table 4, four companies operate four integrated lead smelters/refineries, two lead smelters, and one lead refinery. Each of

TABLE 2. TWENTY-FIVE LEADING LEAD-PRODUCING MINES IN THE UNITED STATES IN 1976, IN ORDER OF OUTPUT (4)

Rank	Mine	County and State	Operator	Source of lead
1	Buick	Iron, Mo.	AMAX Lead Co. of Missouri.	Lead ore
2	Fletcher	Reynolds, Mo.	St. Joe Minerals Corp.	Lead ore
3	Magmont	Iron, Mo.	Cominco American, Inc.	Lead ore
4	Ozark	Reynolds, Mo.	Ozark Lead Co.	Lead ore
5	Brushy Creek	Reynolds, Mo.	St. Joe Minerals Corp.	Lead ore
6	Viburnum No. 29	Washington, Mo.	St. Joe Minerals Corp.	Lead ore
7	Viburnum No. 28	Iron, Mo.	St. Joe Minerals Corp.	Lead ore
8	Indian Creek	Washington, Mo.	St. Joe Minerals Corp.	Lead ore
9	Lucky Friday	Shoshone, Idaho	Hecla Mining Co.	Lead ore
10	Bunker Hill	Shoshone, Idaho	The Bunker Hill Co.	Lead-zinc ore
11	Star Unit	Shoshone, Idaho	Hecla Mining Co.	Lead-zinc ore
12	Ontario	Summit, Utah	Park City Ventures	Lead-zinc ore
13	Viburnum No. 27	Crawford, Mo.	St. Joe Minerals Corp.	Lead ore
14	Leadville Unit	Lake, Colo.	ASARCO, Inc.	Lead-zinc ore
15	Idarado	Ouray and San Miguel, Colo.	Idarado Mining Co.	Copper-lead-zinc ore
16	Burgin	Utah, Utah	Kennecott Copper Corp.	Lead-zinc ore
17	Sunnyside	San Juan, Colo.	Standard Metals Corp.	Lead-zinc ore
18	Balmat	St. Lawrence, N.Y.	St. Joe Minerals Corp.	Zinc ore
19	Ground Hog	Grant, N. Mex.	ASARCO, Inc.	Zinc ore
20	Bulldog Mountain	Mineral, Colo.	Homestake Mining Co.	Silver ore
21	Camp Bird	Ouray, Colo.	Federal Resources Corp.	Lead-zinc ore
22	Pend Oreille	Pend Oreille, Wash.	The Bunker Hill Co.	Lead-zinc ore
23	Austinville and Ivanhoe	Wythe, Va.	The New Jersey Zinc Co.	Zinc ore
24	Eagle	Eagle, Colo.	The New Jersey Zinc Co.	Zinc and silver ore
25	Emperius	Mineral, Colo.	Minerals Engineering Co.	Lead-zinc ore

TABLE 3. PRINCIPAL STATISTICS FOR THE PRIMARY LEAD INDUSTRY IN THE UNITED STATES IN 1978 (3)

Primary lead produced, metric tons	
Mine (recoverable)	529,661
Refinery (refined lead)	566,417
Refinery (antimonial lead, lead content)	4,296
Exports, metric tons	
Lead materials excluding scrap (lead content)	8,225
Lead ore and concentrates (lead content)	54,231
Imports, metric tons	
Ores and concentrates (lead content)	52,985
Refined metal	225,620
Consumption, metric tons	
Reported	1,432,744

TABLE 4. U.S. PRIMARY LEAD PRODUCERS

Company	Location	Description	Capacity, metric ton/year
AMAX-Homestake Lead Tollers	Boss, Missouri	Smelter/refinery[a]	127,000
ASARCO, Inc.	East Helena, Montana	Smelter	109,000
	El Paso, Texas	Smelter	109,000
	Glover, Missouri	Smelter/refinery[a]	100,000
	Omaha, Nebraska	Refinery	163,000
The Bunker Hill Company	Kellogg, Idaho	Smelter/refinery	118,000
St. Joe Minerals Corporation	Herculaneum, Missouri	Smelter/refinery[a]	204,000

[a] The smelting and refining of Missouri lead ore is conducted in the same plant.

these companies also operates a zinc smelter; however, the zinc and lead operations are not located near each other except in Kellogg, Idaho. Figure 1 indicates the locations of domestic primary lead smelters and refineries.

In 1978 approximately 2,400 persons were employed at lead smelters and refineries. Approximately 4700 persons were employed at domestic mines and mills producing lead, lead-silver, or lead-zinc ores or concentrates (3).

Many of the companies producing primary lead are vertically integrated and therefore are involved in two or more process segments. These firms may process other metals such as zinc, copper, and gold, with recovery of these metals often making the mining and processing of lead economically feasible.

Environmental Impact

The primary lead industry emits fine particulate and sulfur dioxide to the atmosphere. The particulate contains metals such as lead, cadmium, and arsenic and originates from sinter machines, blast furnaces, slag fuming, drossing, cadmium recovery, reverberatory softening, and antimony recovery operations. Control of sulfur dioxide emissions is a significant problem for the industry because of all the sources only one gas stream produced by the sintering machine is amenable to sulfuric acid production.

Unlike the copper industry, most lead smelters are located in areas where rainfall exceeds evaporation and consequently recycle of process waters is not completely practicable. Therefore, water pollution can be a problem at lead mines, mills, and smelters. Toxic flotation agents may be discharged from mills, and runoff from smelter property can contain heavy metals. Holding ponds are used for treatment of these waste streams; however, some escape is inevitable.

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Figure 1. Primary U.S. lead smelting and refining locations.

INDUSTRY ANALYSIS

This industry analysis examines each production process to define its purpose and its environmental effects. Each process is analyzed as follows:

1. Function
2. Input Materials
3. Operating Conditions
4. Utilities
5. Waste Streams
6. Control Technology
7. EPA Classification Code
8. References

This section includes only the processes that are now operating in the United States or that are under construction. Figure 2 is a flowsheet showing the processes, their interrelationships, and their major waste streams.

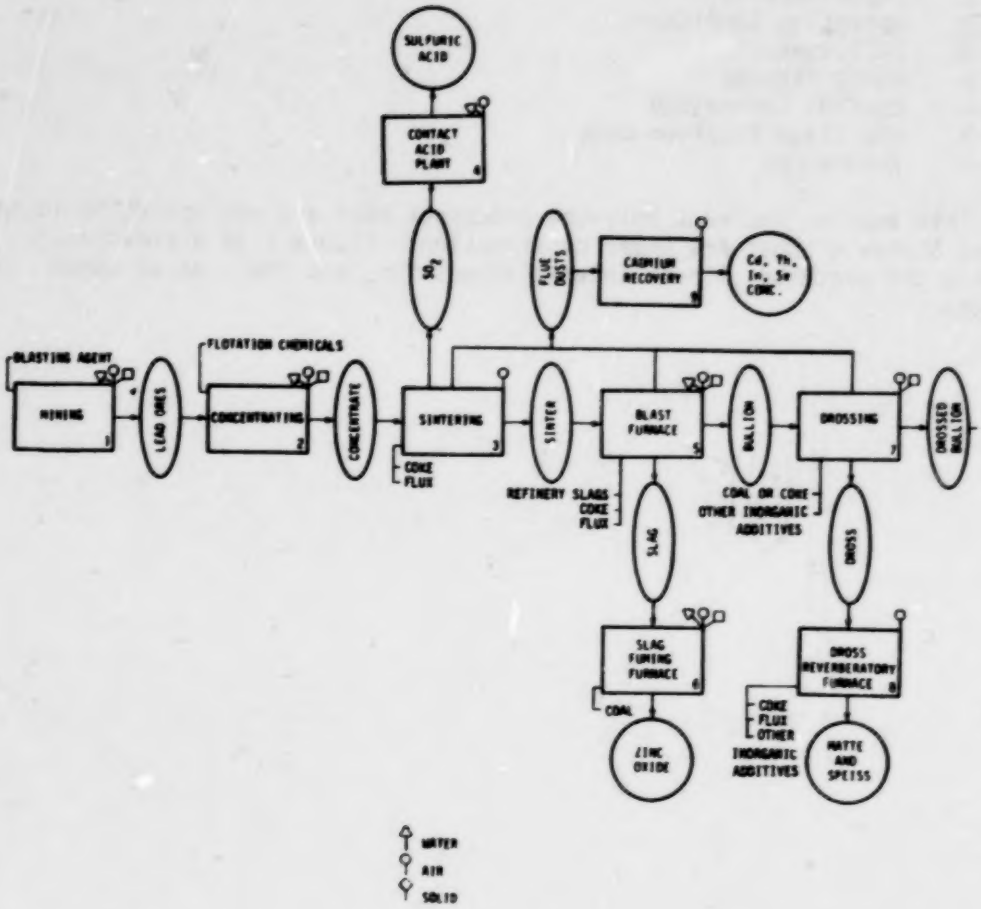

Figure 2. Lead industry flowsheet.

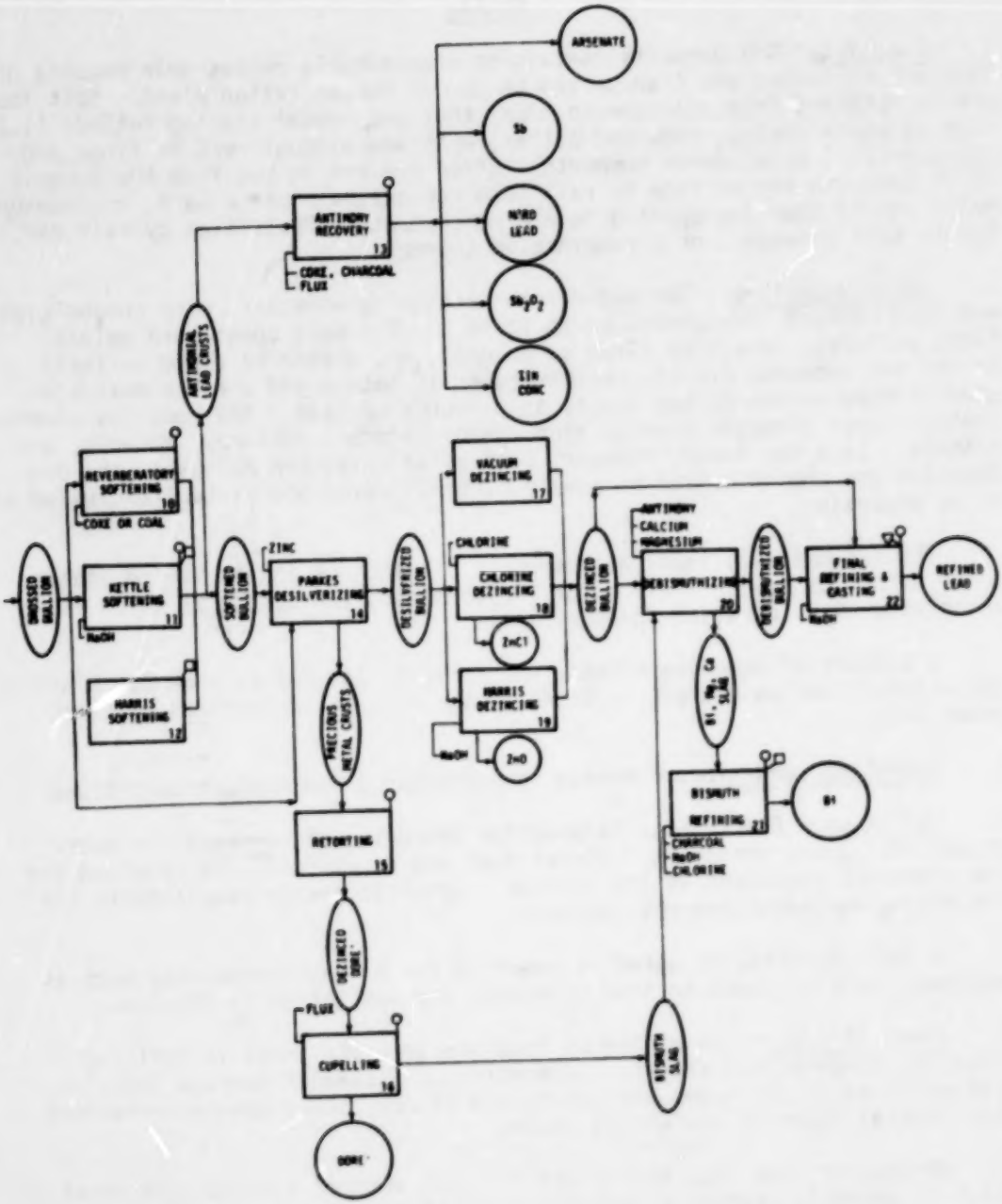

Figure 2 (continued)

Mining

1. Function - Ore deposits containing economically recoverable amounts of lead are excavated and transported to an ore concentration plant. Most lead ore is obtained from underground mines that use normal stoping methods (1,2) such as block caving; room-and-pillar, with and without rock bolting; and cut-and-fill, with timber supports. After the ore is cut from the deposit, it is taken to the surface by rail tram, trackless shuttle cars, or conveyor belts and is then transported to ore concentrating facilities by rail car, truck, belt conveyor, or a combination thereof.

2. Input Materials - The major lead-containing minerals, with composition and lead content, are presented in Table 1. The most common are galena (lead sulfide), cerussite (lead carbonate), and anglesite (lead sulfate). Galena ore deposits are the most abundant in nature and are the most frequently used in the United States as a source of lead. The deposits usually contain other elements such as zinc, gold, cadmium, antimony, arsenic, and bismuth. In a few areas, however, such as southeastern Missouri, the ore deposits are characterized by simple mineralization and virtual exclusion of other minerals.

The economically important deposits of lead ore in the United States occur either as cavity fillings or replacements, the origin of which is associated with intrusive igneous masses.

A mixture of ammonium nitrate and fuel oil (AN-FO) is used for blasting operations. Sodium nitrate is added to the mixture to increase blasting power (3).

3. Operating Conditions - Mining is performed under ambient conditions.

4. Utilities - Electricity is used for operation of equipment in underground mining and transport. Diesel fuel and electricity are required for ore transport equipment at the surface. Specific energy requirements for the mining equipment are not reported.

A small quantity of water is required for miscellaneous uses such as equipment washing, dust control spraying, and sanitation facilities.

5. Waste Streams - The mining of lead ore generates dust in drilling, blasting, loading, and transport operations. Estimated average fugitive dust emission is 110 grams per metric ton of ore, based upon observations from several types of nonferrous mining.

Wastewater from lead mining results from several sources, the worst of which is probably seepage of surface water through spoil piles; others include interception of aquifers and water sent into the mine for utility purposes (5,6). The water is pumped from the mine at a rate necessary to maintain mining operations. The required pumping rate bears no relation to

the ore output and is subject to seasonal variation. The rate can range from a few cubic meters to thousands of cubic meters per day.

Along with small amounts of oil and hydraulic fluid resulting from spills or leaks, the wastewater contains dissolved and suspended solids that reflect the composition of the ore being mined. Analysis of wastewater from a Missouri and an Idaho mine are given in Tables 5 and 6. In general, chemical characteristics of the water are typical of those from any sulfide mine in the same geographic area.

Substantial amounts of solid waste result from underground mining operations, the estimated average for 1973 being 0.13 ton per ton of ore mined (4). This waste material consists of the country-rock surrounding the ore body plus low-grade lead ore contained in it. The normal method of disposal is to pile this waste in a location near the mouth of the mine.

6. Control Technology - Fugitive dust emissions are controlled by the manual use of water sprays or oil as needed.

Wastewater is generally treated with lime and impounded as practiced in copper mining. Since water from Missouri mines is already basic, liming may not be required for pH adjustment. Water from western lead mines is acidic and is treated similarly to that from copper mines. After treatment, the wastewater is reused in ore milling operations.

The solid waste or spoil generated by the mining operation is often used as support and landfill material for highway construction. When it cannot be so used, it is placed in a waste dump located so that it should not contaminate a stream or underground aquifer. Prevention of water seepage is important in this regard.

7. EPA Source Classification Code - None

8. References -

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TABLE 5. ANALYSIS OF A MISSOURI MINE WATER (7,8)

Component	Concentration, mg/l
Mercury	0.001 to 0.002
Cadmium	<0.002 to 0.058
Chromium	<0.010 to 0.17
Manganese	<0.02 to 57.2
Iron	<0.02 to 2.5
Sulfate	63.5 to 750
Chloride	<0.01 to 57
Fluoride	0.063 to 1.2

TABLE 6. ANALYSIS OF AN IDAHO MINE WATER (6)

Constituent	Concentration, ppm	Constituent	Concentration, ppm
pH	2.2	Magnesium	1,500.0
Sulfate as $SO_4^=$	63,000.0	Calcium	31.6
Total iron	16,250.0	Potassium	0.7
Zinc	14,560.0	Sodium	0.5
Nickel	4.8	Chromium	0.3
Copper	13.4	Chloride	38.0
Manganese	2,625.0	Nitrate as $NO_3^=$	77.5
Aluminum	347.0	Electrical conductivity (micromhos @ 25°C)	48,000.0
Lead	0.8		
Cadmium	22.5		

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Concentrating

1. Function - Concentrating is the process whereby the lead-containing portions of the ore produced by the mine are isolated from the fractions low in desirable mineral content. Except for high-grade galena ore produced in southeastern Missouri, ore concentration is required to produce feed material suitable for subsequent metal recovery processes. The process consists of milling the ore by crushing and grinding, followed by separation into two or more fractions. The fractions rich in desired minerals are called concentrates, and the fractions low in mineral content are called gangue.

Separation is achieved by gravity and froth flotation methods. The gravity method achieves separation because of differences in specific gravity of the lead-rich minerals and the gangue particles. The flotation method achieves separation by the use of compressed air and chemical additives that create a froth in which finely divided mineral particles are floated from the gangue. In some applications, the flotation method serves as a supplement to gravity separation to improve the concentrate.

Lead producers of the Mississippi Valley and the eastern United States use gravity separation because there are considerable differences in specific gravities of the ore minerals and the gangue. Since the milled ore particles need not be as small as those required for flotation, the milling costs are lower. Two modes of gravity separation are commonly used, jigging and float-sink. In jigging, the crushed ore particles are fed to an agitated, water-filled jigging chamber, where the heavier ore particles gravitate to the bottom and the lighter gangue is displaced to the top and removed. The float-sink mode utilizes a liquid medium, such as an aqueous ferrosilicon suspension, with a specific gravity between that of the lead mineral and the gangue. The mineral particles sink, while the gangue floats to the top for removal by skimming.

Flotation is practiced chiefly by lead mines in the western United States. The concentrate recovered from the flotation cells contains 45 to 78 percent lead, the percentage depending on the type and grade of crude ore and its susceptibility to flotation. The concentrate also contains varying amounts of other valuable elements.

Ore concentrate from the flotation cells requires dewatering before shipment to smelters. The slurry is fed to thickeners, and flocculating agents such as alum are added to improve the settling rate and fines collection. The thickened slurry of about 50 percent solids is vacuum-filtered and dried to a product containing 6 to 15 percent moisture (1).

Typical analyses of southeastern Missouri and western lead ore concentrates are presented in Tables 7 and 8, respectively.

TABLE 7. TYPICAL SOUTHEASTERN MISSOURI LEAD CONCENTRATE ANALYSES (1)
(percent by weight)

Ag	Pb	Cu	Zn	Fe	Ni	Co	S	As	Insol	CaO	MgO
1.42	74.8	0.64	1.05	2.08	0.10	0.06	15.1	0.009	1.1	1.34	0.90
1.4	76.1	0.85	1.29	1.04	0.2	0.08	15.4	0.006	1.3	0.94	0.75

TABLE 8. WESTERN LEAD CONCENTRATE ANALYSES (4)

Constituent	Percent	Constituent	Percent, weight[a]
Pb	45-60	Sb	0.01-2.0
Zn	0-15	Fe	1.0-8.0
Au	0-0.05 kg/ton	insolubles	0.5-4.0
Ag	0-1.4 kg/ton	CaO	tr-3.0
Cu	0-3	S	10-30
As	0.01-0.40	Bi	tr-0.1

[a] tr = trace.

2. Input Materials - Lead content of the sulfide ores fed to concentrating plants ranges from 3 to 8 percent, except for the high-grade Missouri ores in which lead content exceeds 70 percent (2).

Table 9 lists the flotation chemicals and amounts required for processing lead ore; included also are some of the less commonly used agents.

3. Operating Conditions - All concentrating operations take place at atmospheric pressure and ambient temperatures.

4. Utilities - Water usage varies with the degree of processing and is approximately 4 cubic meters per metric ton of ore processed (3).

Electricity is used to operate grinding equipment and generate compressed air.

5. Waste Streams - Fugitive dust emissions are the only type of atmospheric pollutant warranting consideration. Compositions of the dust are not specified. Crushing operations generate, on the average, 3.2 kilograms of particulate emissions per metric ton of ore processed; 0.9 kilogram is attributable to the crushing and grinding operations, and 2.3 kilograms to material transport and storage (3,4,5).

Liquid waste from the concentrating operation is in the form of a tailings slurry discharged to the tailings pond. Approximately 4 cubic meters of tailings slurry is discharged per metric ton of ore processed (3,6).

Flotation and conditioning chemicals are present in the wastewater either as a floating layer or a solute. In general, lead sulfide flotation is run at an elevated pH level (8.5 to 11) requiring frequent pH adjustments with hydrated lime or sodium carbonate (7). This alkaline wastewater dissolves only small amounts of heavy metals, but can carry mineral particles in suspension.

Wastewaters leaving a concentrating operation contained metals as shown in Table 10. These were the only metals investigated; others may have been present in greater than normal concentrations. Concentrations of calcium, magnesium, sodium, and potassium in mill waters are significantly higher than those in surface water.

Water content of the gangue material from flotation is adjusted to facilitate hydraulic transport to a tailings pond. Tailings contain residual solids from the ore, dissolved solids, and excess mill reagents. Typical quantities are 0.9 to 1.1 tons per ton of ore milled. The main component is dolomite, with small quantities of such constituents as lead, zinc, copper, mercury, cadmium, manganese, chromium, and iron.

6. Control Technology - Dust from the crushing operations is generally reduced by drawing air through the equipment and collecting the dust with cyclone separators. This is both a dust control and an integral part of the process since it allows these small particles to bypass one or more crushing

TABLE 9. FLOTATION CHEMICALS (8)

Chemical	Amount used, kg/metric ton of ore
Na_2CO_3 (conditioner)	0.45 - 0.9
CaO (conditioner)	0.9 - 18.
$CuSO_4$ (activator)	0.36 - 0.55
Sodium isopropol xanthate (collector)	0.0045 - 0.09
Pine oil (frothers)	0.09
NaCN (depressant)	0.045 - 0.14

LESS COMMON FLOTATION REAGENTS

Reagent	Purpose
Methyl isobutyl-carbinol	Frother
Propylene glycol methyl ether	Frother
Long-chain aliphatic alcohols	Frother
Potassium amyl xanthate	Collector
Dixanthogen	Collector
Isopropyl ethyl thionocarbonate	Collectors
Sodium diethyl-dithiophosphate	Collectors
Zinc sulfate	Zinc depressant
Sodium dichromate	Lead depressant
Sulfur dioxide	Lead depressant
Starch	Lead depressant

TABLE 10. LEAD MILL WASTEWATER ANALYSIS (6)

Component	Concentration, mg/l
Mercury	<0.001
Lead	0.107 to 1.9
Zinc	0.12 to 0.46
Copper	0.014 to 0.36
Cadmium	0.005 to 0.011
Chromium	0.002 to 0.02
Manganese	0.03 to 0.169
Iron	0.03 to 0.53

and grinding operations. Fugitive dust is usually uncontrolled unless the amount being lost economically justifies the installation of equipment for its recovery.

To preserve the Ozark area of Missouri where the New Lead Belt is located, special attention has been given to wastewater treatment. Flotation reagents in the wastewater are biologically degraded by algae growth. Use of meandering streams before final discharge to receiving waters increases exposure to the algae and provides good conditions for algae growth. The algae sink to the bottom of the stream and act as a solids collector, as well (6). Disposal of algae in event of excessive growth is not discussed in the literature.

7. EPA Source Classification Code - 3-03-010-04

8. References -

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Sintering

1. Function - The ore concentrate is treated by sintering to make it suitable for subsequent blast furnace operation. Sintering is the roasting of blended and pelletized ore concentrate mixtures. The purposes of sintering are as follows:

1) To provide a feed of proper ratio of lead, silica, sulfur, and iron for smelting;

2) To convert metallic oxides into oxides or sulfates amenable to smelting;

3) To drive off volatile oxides such as SO_2, SO_3, As_2O_3, and Sb_2O_3; and

4) To produce a firm, porous clinker that is easily fed to a blast furnace (1).

The process consists of three consecutive steps:

1) Blending of ore concentrates with direct-smelting ores, sinter recycle, flue dust, and fluxes;

2) Pelletization of the blended mixture; and

3) Roasting of pelleted material.

Blending balances the smelter charge and permits control of impurity levels of zinc, copper, arsenic, antimony, and bismuth. Pelletizing is achieved by mixing the blended charge with 6 to 8 percent by weight water in a pug mill and feeding the mix to a rotating pelletizing drum. Resulting pellets are 3 to 5 millimeters in diameter.

The pellets are spread evenly over a horizontal metal belt which takes them through an updraft sintering machine. The only remaining downdraft sintering machine was scheduled for replacement early in 1979. As the pellets proceed through the sintering machine, they are heated and undergo oxidizing reactions that convert sulfides to oxides and sulfates. Lead silicate forms, and oxides combine to form low-melting-point silicate complexes, which bind the ore particles together.

The resulting sinter is broken into pieces ranging up to 25 millimeters diameter (2). The crushed sinter is screened for removal of fines, which are recycled to the charge blending step. The screened product is stored for blast furnace reduction. Table 11 gives typical ranges of components in the sintered product.

TABLE 11. SINTER ANALYSIS (1,3,4)

Component	Weight, percent
Ag	0.03-0.07
Cu	0.3-4.5
Pb	28-50.0
S	0.75-2.0
Fe	12-15.5
SiO_2	10.0-15.6
CaO	9.0-10.5
Zn	4.0-12.5
Sb	0.01-1.5
Cd	Tr-0.04

2. Input Material - Lead concentrates are the main input material for sintering. Typical analyses of western and Missouri lead concentrates are presented in the concentrating process description (Process No. 2). Collected flue dusts, recycled sinter, and smelter residues also are part of the charge for sintering. Sulfide-free fluxes are added to maintain a specified sulfur content (5 to 7 percent by weight) in the charge. Silica and limestone are used as needed. Coke fines, in the amount of 1 percent by weight of the total charge, are mixed with the charge (5).

Typical feed sources to a sinter machine are presented in Table 12.

TABLE 12. SINTER MACHINE FEED (10)

	Weight, percent
Ore concentrate	31.47
Misc. lead materials	12.44
Flux diluent	19.86
Sinter recycle	36.20

3. Operating Conditions - Temperatures in both updraft and downdraft sinter roasting machines reach approximately 800°C. Pressure is atmospheric.

4. Utilities - In updraft sintering machines gas- or oil-fired burners are used to ignite the charge. Energy consumed in the sintering process amounts to 0.5 million kilocalories per ton of lead produced. A breakdown allocates 40 percent to coke consumption and 60 percent to gas or oil consumption, gas being used more than oil (6).

Water may be added for pelletizing the charge if the moisture content is below required limits. Air is injected through the charge while oxidizing in the sintering machines. No quantities are given for air injection.

Electricity is the power source for fans, feed conveyors, and general operating equipment. Approximately 20 percent less power is required for the updraft fans than for downdraft (7).

5. Waste Streams - Particulate emissions are approximately 100 to 250 kilograms per metric ton of lead produced in sinter machines (9). Analysis of the flue dust shows roughly 40 to 70 percent lead, 10 to 20 percent zinc, and 8 to 12 percent sulfur (8). Depending upon concentrate composition, the flue dust contains various amounts of antimony, cadmium, germanium, selenium, tellurium, indium, thallium, chlorine, fluorine, and arsenic (7). Tables 13 and 14 give weight analysis and size distribution of particulate emissions.

TABLE 13. GRAIN LOADING AND WEIGHT ANALYSIS OF INPUT FEED AND EMISSIONS UPDRAFT LEAD SINTERING MACHINE (11)

Grain loading, g/Nm^3 (0°C)	Weight analysis, %	
16.3	Pb	35-50
	SiO_2	8-11
	Fe	9-13
	CaO	7-10
	MgO	0.7-1
	Zn	4-6
	S	0.7-1
	Cu	tr
	As	tr-30
	Cd	tr
	Se	tr
	inerts	6-8

TABLE 14. TYPICAL SIZE PROFILE OF EMISSIONS, UPDRAFT LEAD SINTERING MACHINE (11)

Size, micron	% weight
20-40	15-45
10-20	9-30
5-10	4-19
< 5	1-10

Sintering is the only step in the lead smelting process that emits enough SO_2 to create a serious air pollution control problem. About 85 percent of the sulfur is removed from the concentrate during sintering. Approximately 50 percent of the remainder is discharged as SO_2 from subsequent operations; the balance goes into the slag as sulfates (7,9).

In the sintering process most of the sulfur is eliminated at the front end of the conveyor. By the time the charge reaches the end of the machine, little SO_2 is being emitted. If the exit gases are removed in a single stream, the SO_2 concentration is about 2 percent (7,8). In an updraft machine, the exit gases can be split into two streams, one predominantly from the front and the other from the rear. This procedure produces both a weak and a strong SO_2 stream, 0.5 and 5.7 percent SO_2 respectively (7).

Off-gases also contain organic vapors from flotation reagents or their combustion products. The compounds formed from these flotation chemicals by reactions caused by the sintering temperatures are not known. Traces of HF and SiF_4 may be found in these gases. The volume of gases emitted is a function of machine size and material throughput and ranges from 0.25 to 0.50 normal cubic meters per minute per square meter of bed area (8). Temperatures of the gases normally range from 150° to 400°C (5,8). Flow rates may vary between 58,000 and 66,000 standard cubic meters per hour (8).

Table 15 gives a typical analysis of gases from a sintering machine. A small but variable amount of arsenic trioxide in the gaseous form may also be present.

6. Control Technology - Particulates from the sinter machine are collected by several different methods. Table 16 lists current atmospheric controls on lead sintering processes. Efficiencies range from 95 to 99.8 percent.

The strong gas stream collected from separation of updraft exit gases is the only stream amenable to sulfuric acid production. In both the weak stream and the combined single stream, concentrations are too low for such treatment. At least one smelter has installed a recirculation system for the weak stream, which allows SO_2 to be removed in the strong stream exit for subsequent treatment. Certain foreign operations have successfully made use of this technique for some time.

Three plants are now controlling SO_2 in sinter machine off-gases by use of single-contact sulfuric acid plants, which reduce total SO_2 emissions by 70 to 80 percent. Another plant is planning to add an acid plant to its new updraft machine.

Currently no lead smelters practice control on weak SO_2 streams. The best available control technology for these streams would be chemical scrubbing.

TABLE 15. ANALYSIS OF SINTER MACHINE EXHAUST GASES (MISSOURI LEAD OPERATING COMPANY) (12)

	Range, % by volume
SO_2	4-7
O_2	4-9
CO_2	3-4
N_2	84-85
SO_3	0.05-0.2
Dust content	57 g/Nm^3
Temperature	200-350°C
Moisture content	25 percent by vol.

TABLE 16. ATMOSPHERIC CONTROL SYSTEMS ON PRIMARY LEAD SINTERING MACHINES (7)

Plant	Control system
Bunker Hill/Kellogg, Idaho	Updraft sintering machine produces two gas streams: strong gas stream to acid plant. Weak gas stream combined with blast furnace and hygiene air, then goes to a baghouse and out the stack.
AMAX/Boss, Missouri	Updraft sintering machine produces two gas streams: strong gas stream to acid plant. Weak gas stream combined with blast furnace gas before discharge through stack.
St. Joe/Herculaneum, Missouri	Updraft sintering machine produces two gas streams: strong gas stream to acid plant. Weak gas stream joins other gases, then thru baghouses and to stack.
ASARCO/E. Helena, Montana	Updraft sintering machine. Gases to water spray, ESP, then dilution air added and released to stack.
ASARCO/Glover, Missouri	Updraft sintering machine. All gases to water spray and baghouse, then out stack.
ASARCO/El Paso, Texas	Updraft sintering machine. A new control system is planned, making use of an acid plant for the strong stream.

7. EPA Classification Code - 3-03-010-01.

8. References -

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Contact Sulfuric Acid Plant

1. Function - An acid plant catalytically oxidizes SO_2 gas to sulfur trioxide, and absorbs it in water to form sulfuric acid. The sintering machine produces the only lead smelter exit gases that are amenable to production of sulfuric acid.

Contact sulfuric acid plants are continuous steady-state processing units that are operated in other industries using SO_2 made by burning elemental sulfur. They may be used with waste SO_2 streams if the gas is sufficiently concentrated, is supplied at a reasonably uniform rate, and is free from impurities.

The heart of a sulfuric acid plant is a fixed bed of vanadium pentoxide or other special catalyst which oxidizes the SO_2. All other components of the plant are auxiliary to this catalytic converter. The other components clean and dry the stream of gas, mix the proper amount of oxygen with it (unless sufficient oxygen is present), preheat the gas to reaction temperature, and remove the heat produced by the oxidation.

The plant incorporates one or two absorbers to contact the gas with water to form the acid. If only one absorber is provided, this is described as a single-contact sulfuric acid plant. If two are provided, the second is placed between stages of the converter, and this is a double-contact plant. The second absorber allows a larger proportion of the SO_2 to be converted into acid, and thus removes more SO_2 from the gas stream if the initial concentration is high.

2. Input Materials - Most contact sulfuric acid plants operate most efficiently with a constant gas stream that contains 12 to 15 percent SO_2. Performance almost as good can be achieved in plants that are designed for 7 to 10 percent SO_2 content. The ability of a plant to convert most of the SO_2 to sulfuric acid declines either as gas streams become weaker in SO_2 or as the flow rate or concentration becomes less consistent. A concentration lower than 4 percent SO_2 is extremely inefficient, since sufficient catalyst temperature cannot be maintained (1). Certain modifications of the process, which add heat by combustion of fuel, can provide better conversion at low SO_2 concentrations.

The gas that enters the catalyst bed must be cleaned of all particulate matter, be almost completely dried, and contain no gases or fumes that act as poisons to the catalyst. The acid plant is always supplied with special scrubbers to remove final traces of objectionable materials.

Clean water is required to react with the SO_3 to form sulfuric acid. It may be necessary to deionize the water in a special ion exchange system in order to avoid excessive corrosion or to meet acid quality specifications. Steam condensate may also be used.

3. Operating Conditions - The catalyst bed operates properly only if temperatures are maintained between 450° and 475°C. Pressures do not usually exceed 2 kilograms per square centimeter. The plants are usually not enclosed in a building.

4. Utilities - Noncontact cooling water is required. At one plant producing 1500 metric tons of acid per day, about 12 million liters of water is required each day (2).

A small amount of electricity is required for pumps and blowers. This may be generated on site in some cases, where recovery of waste heat is maximized.

In certain patented modifications, heat from combustion of natural gas is used to provide better efficiency at low SO_2 concentrations. Natural gas or oil is also required to heat any acid plant to operating temperature following a shutdown.

5. Waste Streams - Single-contact sulfuric acid plants using weak gas streams can at best absorb only 96 to 98 percent of the SO_2 fed to them. The remaining quantity passes through to the atmosphere. Efficiencies as low as 60 percent have been reported (3).

Double-contact acid plants provide a higher percentage of SO_2 removal if they are fed gas with a higher SO_2 content. Efficiencies higher than 99 percent have been reported. Exit gas SO_2 concentration is still usually within the same range as shown above, although one recently developed process claims stack emissions of less than 0.005 percent SO_2 (4).

In sulfuric acid plants, it is difficult to prevent some loss of SO_3, in the form of a fine mist of sulfuric acid, with the absorber exit gases. This is usually 0.02 to 0.04 kilogram of SO_3 per metric ton of 100 percent acid produced.

The scrubbing columns that clean the waste gas stream create off-grade weak acid that cannot be sold. The amount is estimated as 4 to 8 liters for each 10 cubic meters of gas treated (5).

In this industry, most particulate matter from gas cleaning equipment is recycled to the metallurgical processes. The small quantities of particulate removed by the acid scrubbing operations, however, are mixed with a stream of weak sulfuric acid and cannot readily be recycled. They are discharged with the acid plant blowdown.

In some sections of the country it is difficult to sell the product acid, even for less than the cost of manufacture. Therefore, it may be less expensive to neutralize and discard the acid than to absorb the costs of shipment to a distant user. Thus, the product acid can itself become a waste stream.

An acid plant does not produce solid wastes directly, but the gypsum formed in neutralization of acid can constitute a significant solid waste.

6. Control Technology - In this country the SO_2 in the tail gas from the sulfuric acid plant is not controlled. When SO_2 emissions are large, the best control may be to increase operating efficiency by adding additional catalyst stages or by adding heating equipment to maintain proper catalyst temperature. Changes in the metallurgical operations to produce a stream of higher SO_2 concentration at a more uniform rate are also good controls, if this is possible. Scrubbing of the weak SO_2 stream for final SO_2 absorption may also be necessary.

Mist eliminators in the form of packed columns or impingement metal screens can minimize acid mist emissions. Manufacturers claim elimination of all but 35 to 70 milligrams of mist per cubic meter of gas, and the units at times perform better. To prevent formation of plumes of mist during periods of abnormal operations, however, electrostatic precipitators are often used. Better regulation of feed rate and quality also minimizes acid loss.

Tables 17 and 18 give the treatments now practiced at lead smelters for the control of acid plant blowdown and scrubber water (1).

If volumes of strong acid must be neutralized, treatment with limestone is followed by more precise pH adjustment with lime, and discharge to a pond for in-perpetuity storage of the resulting gypsum is the only tested and economical method of disposal.

7. EPA Source Classification Code - None

8. References -

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TABLE 17. WASTEWATER TREATMENT AT PRIMARY LEAD ACID PLANTS (6)

Plant	Liquid effluent treatment	Discharge
1	Enters water treatment plant, limed, thickened, and filtered, and sent to reservoir for recycle.	0
2	Recycled to slag granulation.	0
3	Enters liming sump, then passed to lime bed, then to a cooling pond.	273 m^3/day

TABLE 18. SCRUBBER WASTEWATER TREATMENT AT PRIMARY LEAD PLANTS (6)

Plant	Treatment	Discharge
1	Enters water treatment plant, limed, thickened, filtered, and then sent to reservoir for recycling.	0
2	Recycled from a cooling tower.	0
3	Sent to a lime sump then to a settling pit. Most is recycled.	Undetermined

Blast Furnace

1. Function - Sintered feed is reduced in the blast furnace to produce a crude lead bullion. Specified amounts of coke, limestone, and other fluxing materials are charged with the sinter through a water-jacketed shaft at the top of the furnace. The material settles to the furnace bottom, which is supported by a heavy refractory material.

Air is injected into the charge through side-mounted tuyeres to effect a more complete formation of metallic oxides and thereby raise the temperature of the charge. At the operating temperature of the furnace, coke and resulting carbon monoxide reduce most of the metallic oxides to yield a molten mass of metal. Some of the metallic impurities interact with the flux to form a slag composed mainly of iron and calcium silicates. Depending upon the composition of the charge, material in the blast furnace can separate into as many as four distinct liquid layers.

Copper, if present in lead ores, reacts with residual sulfur to form a matte that separates into a layer beneath the slag. The matte typically assays 44 to 62 weight percent copper, 10 to 20 percent lead, and up to 13 percent sulfur (1). If the charge is high in arsenic and/or antimony content, a speiss layer will form under the matte. Speiss compounds are arsenides and antimonides of iron and other metals. The bottom layer of lead bullion is 94 to 98 weight percent lead plus varying amounts of other metals such as copper, tin, arsenic, antimony, silver, and gold. Typical ranges of composition are shown in Table 19.

Upon completion of the process, the crude bullion is charged to drossing kettles (2), the matte and speiss are sold to a copper smelter, and the slag is discharged to a fuming furnace. A typical slag analysis is shown in Table 20.

The capacity of most large blast furnaces is 1360 metric tons of charge materials per day.

2. Input Materials - The blast furnace charge is made up of sinter, fluxes, coke, and sundry materials recycled from other smelting operations. The relative amounts of these materials are presented in Table 21.

Normally, coke comprises 8 to 15 weight percent of the furnace charge. If the blast air is enriched with oxygen, coke consumption is reduced 10 percent with a 10 to 20 percent increase in smelting rate.

3. Operating Conditions - Temperatures in a blast furnace range from 215°C for the charge near the top of the furnace to 1220°C in the slag zone. Slag temperatures range from 1000° to 1220°C, and bullion temperatures from 900° to 950°C.

Because of the exhaust gas configuration, the blast furnace operates at a pressure slightly above atmospheric.

TABLE 19. LEAD BULLION COMPOSITION (2,3,4)

Component	Wt. percent
Ag	0.13-0.31
Au	1.6-3.1[a]
Cu	1.0-2.5
S	0.25
Pb	94-98
Fe	0.6-0.8
Zn	tr.
Sn	tr.
As	0.7-1.1
Sb	1.0-1.75
Bi	0.01-0.03

[a] Value for Au in g/metric ton.

tr. - trace

TABLE 20. TYPICAL BLAST FURNACE SLAG ANALYSIS (2,3,4)

Component	Weight percent
Ag	1.56-4.69[a]
Cu	0.10[b]
Pb	1.5-3.5
FeO	25.5-31.9
CaO	14.3-17.5
Zn	13.0-17.5
insol	22.6-26.5[d]
MnO	2.0-4.5
As	0.10
Sb	0.10
Cd	0.10
F	tr[c]
Cl	tr[c]
Ge	tr[c]
S	0.5-1.0

[a] Values for Ag in grams per metric ton.

[b] Variable, depending on the furnace charge.

[c] tr = trace.

[d] Insolubles include MgO - AlO - SiO_2 phases.

TABLE 21. TYPICAL BLAST FURNACE CHARGE (2)

Component	Weight, kg
Sinter	1250-1650
Coke	125-165
Miscellaneous products (zinc plant residues)	0-90
Slag (dross)	0-225
Silica	0-36
Limerock	0-27
Cadmium residue	0-9
Refinery dross	0-35
Baghouse product	0-35

4. Utilities - Air is injected into the charge at a pressure of 0.1 to 0.3 kilogram per square centimeter (2). Consumption of 140 to 175 cubic meters per hour is required for a charge of 1360 metric tons per day (2).

Cooling water circulates through jacketed shafts to control furnace temperatures. Quantities are unreported.

5. Waste Streams - Particulate emission rates in blast furnace exhaust gas range from 125 to 180 kilograms per metric ton of bullion produced (3,5). Particle sizes of the dust range from 0.03 to 0.3 micron (5). The dust is composed of oxides, sulfates, and sulfides of the various metals present in the furnace charge, plus chlorides, fluorides, and coke dust (5,6).

Undiluted gas temperatures are estimated to be 650° to 750°C (3,5), with theoretical flue gas rates of 170 to 400 normal cubic meters per minute. After dilution by air and water vapor, however, volume typically increases from 9 to 12 times the theoretical flow (1).

Exhaust gas analysis after air dilution and CO combustion is reported in Table 22.

TABLE 22. EXHAUST GAS ANALYSIS AFTER AIR DILUTION AND CO COMBUSTION (5,7)

Component	Percent by volume
CO_2	15
O_2	15
CO[a]	5
SO_2	0.05
N_2	Remainder

[a] CO concentration estimated to be 25 to 50 volume percent prior to combustion.

Other reports indicate that CO and SO_2 concentrations, although highly variable, average 2.0 and 0.01 to 0.25 volume percent, respectively (1,5). An estimated 10 to 20 weight percent of total sulfur in the feed concentrate is removed in the blast furnace, half emitted as SO_2 and the rest retained in the slag or matte (8).

Slag from the blast furnace is generally discharged and granulated with cooling water.

6. Control Technology - The dilute SO_2 emissions from the blast furnace are not controlled at lead smelters. The best available control technology is chemical scrubbing.

Particulates in blast furnace exhaust gases are controlled at all smelters by means of baghouses. Control efficiency ranges from 95 to 99.9 percent. Table 23 describes controls for blast furnace gases.

Current practice for slag disposal is to convey it hydraulically with the granulating water stream to a dump or tailings pond. Recommended technology includes use of concrete settling pits, ground sealing of disposal area, and diversion of runoff to a water treatment lagoon.

7. EPA Classification Code - 3-03-010-02

8. References -

1. Arthur G. McKee & Co. Systems Study for Control Emissions Primary Nonferrous Smelting Industry. U.S. Department of Health, Education, and Welfare. June 1969.

2. PEDCo-Environmental, Specialists, Inc. Trace Pollutant Emissions from the Processing of Metallic Ores. August 1974.

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4. Development Document for Interim Final Effluent Limitations Guidelines and Proposed New Source Performance Standards for the Lead Segment of the Nonferrous Metals Manufacturing Point Source Category. Environmental Protection Agency. EPA-440/1-75/032-a. February 1975.

5. Jones, H.R. Pollution Control in the Nonferrous Metals Industry. Noyes Data Corporation. Park Ridge, New Jersey. 1972.

6. Phillips, A.J. The World's Most Complex Metallurgy (Copper, Lead, and Zinc). Transactions of the Metallurgical Society of AIME. Volume 224. August 1962. pp. 657-668.

7. Arthur G. McKee & Co. Systems Study for Control of Emissions Primary Nonferrous Smelting Industry. U.S. Department of Health, Education, and Welfare. June 1969.

8. Background Information for New Source Performance Standards: Primary Copper, Zinc, and Lead Smelters. Volume I, Proposed Standards. Environmental Protection Agency, Research Triangle Park, North Carolina. EPA-450/2-74-002a. October 1974.

TABLE 23. ATMOSPHERIC CONTROL SYSTEMS ON PRIMARY LEAD BLAST FURNACES (7)

Plant	Control system
Bunker Hill/Kellogg, Idaho	Blast furnace gas stream joined to weak sinter gas stream and hygiene air, then to baghouse then to stack.
AMAX/Boss, Missouri	Blast furnace gases join sinter weak gases, then to baghouse, and then out the stack.
St. Joe/Herculaneum, Missouri	Blast furnace gases join sinter weak gases and other gases pass thru baghouses and stack.
ASARCO/E. Helena, Montana	Blast furnace gases join reverb and ventilation gases, then pass thru three baghouses in parallel with stack for each house.
ASARCO/Glover, Missouri	Blast furnace gases to water spray, baghouse, and three stacks.
ASARCO/El Paso, Texas	Blast furnace and dross furnace gases mix, then pass thru a spray chamber and a baghouse, then out six stacks.

Slag Fuming Furnace

1. Function - A slag fuming furnace is used to recover metal values otherwise lost in the slag. Blast furnace slag contains appreciable concentrations of lead and zinc oxides created through reoxidation of the metals in the bottom portion of the blast furnace.

The slag is fed to the fume furnace in the molten state, and pulverized coal is used with a stream of primary combustion air to supply heat and to maintain a reducing environment. The metallic oxides are first converted to metals, then are reoxidized with a stream of secondary air added above the slag surface. Lead and zinc are discharged from the slag fuming furnace as finely divided particulates entrained in the furnace gases.

A matte is sometimes separated from the slag in this operation for recovery of substantial amounts of copper and silver from the dezinced slag. When fuming has subsided, the slag is dumped and cooled with water.

2. Input Materials - Composition of the blast furnace slag charged to the fume furnace is shown in Table 20 of Process No. 5. Two tons of slag are generated per ton of crude lead bullion produced by the blast furnace. Pulverized coal is added to maintain temperature by combustion. The amount is not specified in the literature.

3. Operating Conditions - The slag temperature range is 1000° to 1200°C. Atmospheric pressure is used (1).

4. Utilities - Air is injected into the furnace for combustion of the coal. Quantities are not cited in the literature (2).

Water is used for slag cooling and granulation in amounts ranging from 200 to 8,200 cubic meters per day (3), the amount depending upon the design of cooling water circuit at a given plant. A typical analysis is given in Table 24.

5. Waste Streams - The exhaust gas from the furnace typically has a low SO_2 concentration. The literature (2) cites a value of 0.02 volume percent for a flow rate of 5,660 normal cubic meters per minute. Gas stream temperature is about 1200°C.

The exit gas also contains high concentrations of particulate and fume composed of the volatile components of the blast furnace slag. The literature does not cite quantities or composition.

The dumped slag and water used for granulation constitute the major waste stream from the process. The slag is made up of various compounds of iron, calcium, silicon, aluminum, magnesium, and other elements. The water-soluble portions are leached by the cooling water. Table 24 presents analyses of the intake and outflow streams of water used for slag granulation.

TABLE 24. WASTE EFFLUENTS FROM SLAG GRANULATION

Parameter	Total plant intake mg/l	Total plant discharge mg/l	Net change, mg/l	Net loading kg/ton
pH	7.6	8.3	-	-
Alkalinity	203	186	-17	NLC[a]
COD	8	8	0	0
Total solids	-	-	-	-
Dissolved solids	408	500	92	0.89
Suspended solids	3	36	33	.32
Oil and grease	-	-	-	-
Sulfate (as S)	145	215	70	0.67
Chloride	18	-	-	-
Cyanide	-	-	-	-
Aluminum	-	-	-	-
Arsenic	-	-	-	-
Cadmium	-	-	-	-
Calcium	70	-	-	-
Chromium	-	-	-	-
Copper	0.02	0.02	0	0
Iron	1.70	-	-	-
Lead	0.12	0.30	0.18	0.0018
Magnesium	.31	-	-	-
Mercury	-	-	-	-
Molybdenum	-	-	-	-
Nickel	0.03	0.04	0.02	0.00018
Potassium	-	-	-	-
Selenium	-	-	-	-
Silver	-	-	-	-
Sodium	-	-	-	-
Tellurium	-	-	-	-
Zinc	0.05	0.12	0.38	0.0037

Process water flow: 6 million liters/day.

Production: 695 metric tons/day.

Source: This contract and 1971 RAPP data.

Notes:

[a] NLC = no load calculable.

6. Control Technology - The exhaust gas from the fuming furnace is cooled by waste heat boilers or cooling chambers before being sent to baghouses for removal of particulate and condensed volatiles. Baghouse operation is limited to a maximum temperature of 285°C. Particulate removal efficiency ranges from 95 to 99 percent (4). It is preferable to operate the baghouse at the lowest possible temperature to allow removal of volatile matter contained in the gas stream.

Slag disposal is the same as described in Process No. 5, involving conveyance with the granulating water stream to a dump or tailings pond, use of concrete settling pits, ground sealing, and diversion of runoff.

Normally, it is desirable to recycle slag granulation water after cooling and clarification. A smaller stream is bled off to neighboring surface water to control buildup of water-soluble components. The best available control technology for wastewater treatment is a combination of neutralization and clarification; the resulting effluent concentrations are presented in Table 25. The control methods in use are presented in Table 26.

TABLE 25. EFFLUENT CONCENTRATIONS WITH NEUTRALIZATION AND CLARIFICATION

Component	Concentration, mg/l
Cadmium	0.5
Lead	0.5
Mercury	0.005
Zinc	5.0

These values are currently being met by five of the six lead smelters.

7. EPA Classification Code - None

8. References -

1. Encyclopedia of Chemical Technology. Interscience Publishers, a division of John Wiley and Sons, Inc. New York. 1967.

2. Arthur G. McKee & Co. Systems Study for Control of Emissions Primary Nonferrous Smelting Industry. U.S. Department of Health, Education, and Welfare. June 1969.

3. Hallowell, J.B., et al. Water Pollution Control in the Primary Nonferrous Metals Industry. Volume I, Copper, Zinc, and Lead Industries. Environmental Protection Agency. Washington, D.C. EPA-R2-73-274a. September 1973.

TABLE 26. PRIMARY LEAD SLAG GRANULATION
WASTEWATER TREATMENT (5)

Plant	Treatment	Discharge
1	Sent to cooling pond.	8,230 m^3/day (2,200,000 gpd)
2	Sent to settling pit then to a cooling pond.	273 m^3/day (72,000 gpd)
3	Sent to settling pond and recycled.	0
4	Sent to two settling ponds in series.	Discharge is present but no quantities are available.
5	Sent to a slag pile.	No apparent discharge to surface. Leaching is not mentioned.
6	No data.	No data

4. Vandergrift, A.E., L.J. Shannon, P.G. Gorman, E.W. Lawless, E.E. Salle, and M. Reichel. Particulate Pollutant System Study - Mass Emissions, Volumes 1, 2, and 3. U.S. Environmental Protection Agency (NTIS). Durham, North Carolina. PB-203 128, PB-203 522, and PB-203 521. May 1971.

5. Development Document for Interim Final Effluent Limitations Guidelines and Proposed New Source Performance Standards for the Lead Segment of the Nonferrous Metals Manufacturing Point Source Category. Environmental Protection Agency. EPA-440/1-75/032-a. February 1975.

Drossing

1. Function - Drossing is the initial step in refining lead bullion. Molten bullion from the blast furnace is placed into drossing kettles of 90 metric-ton capacity where submerged air lances provide agitation and oxidation. The kettle and molten bullion are cooled to a temperature at which lead is still a liquid but oxides of the common impurities and oxides of lead solidify. The term "dross" refers to any solid scum floating on top of a metal bath. Dross may contain varying amounts of lead, copper, tin, indium, arsenic, antimony, and bismuth. Because of the high specific gravity of molten lead, these solid oxides float and are easily skimmed off the molten lead. Drossing of the blast furnace bullion always occurs before the lead is sent to the refinery.

For more complete removal of copper, sulfur is added to the drossing kettle. This sulfur combines with the remaining copper forming cuprous sulfide (CU_2S), which floats and is skimmed off with the rest of the dross. By drossing, a bullion with copper content as high as 2 percent can be reduced to approximately 0.005 percent copper (1).

The dross is sent to a dross reverberatory furnace for further treatment and recovery of marketable products. Dross may typically contain 90 percent lead oxide, 2 percent copper, and 2 percent antimony, in addition to other values such as gold, silver, arsenic, bismuth, indium, zinc, tellurium, nickel, selenium, and sulfur. The collected dross amounts to 10 to 35 percent of the blast furnace bullion (1). A typical assay of drossed bullion is shown in Table 27.

2. Input Materials - Lead bullion is the principal input. During the drossing procedures sulfur is added in a ratio of approximately 1 kilogram per ton of bullion from the blast and dross reverberatory furnace. Various amounts of coal or coke, ammonium chloride, soda ash (Na_2CO_3), and litharge or baghouse fume (PbO) are added to the kettles as needed.

3. Operating Conditions - The molten bullion is cooled to a temperature of 370° to 500°C and maintained within that range. Pressures are atmospheric (1).

4. Utilities - Most of the drossing kettles are heated with natural gas. About 1.1 million kilocalories per metric ton are consumed during this stage, of which 90 percent is allocated to gas and 10 percent to oil (2). Conveyors, agitators, pumps, and similar equipment are powered by electricity. Air is injected by submerged lances for supplementing oxidation and agitation (1,5,6). Quantities of electrical and air consumption are not given in the literature.

5. Waste Streams - The drossing operation generates small amounts of air pollutants and slag. The air pollutants are SO_2 and volatile components of the lead bullion. A typical analysis of the bullion was presented in Table 19. Varying quantities of copper, iron, arsenic, zinc, cadmium, antimony, and bismuth may be volatilized; it is believed that the quantities are very

TABLE 27. LEAD BULLION ANALYSIS (1,3,4)
Basis: As drossed

Element	Wt. percent
Ni	tr.
Ag	0.13-0.31
Au	1.2-3.1[a]
Cu	0.08-0.005
Fe	0.7-0.8
Te	0.01-0.03
As	0.7-1.1
Sb	1.0-1.75
Bi	0.01-0.03
Se	tr.
Sn	tr.

[a] Value of Au in g/metric ton.
tr. = trace.

small because of the low temperatures. The SO_2 content of the off-gas is very low, usually less than 0.05 percent by volume. Flow rates of exit gases from a blast furnace are typically 5,100 to 5,500 normal cubic meters per minute. Temperatures of these gases are low, approximately 200° to 300°C (6). The particulate loading has been quantified by one source as being between 1.0 and 21.7 grams per cubic meter of off-gas (7). Another source cites the emission rate as 10 kilograms per metric ton of lead produced.

6. Control Technology - No control methods are presently applied to the weak SO_2 stream emitted from the drossing operation. The best available technology is chemical scrubbing.

Particulates and fumes from the drossing kettles are combined with the blast furnace off-gas at all plants. See Process No. 5.

7. EPA Source Classification Code - None

8. References -

1. Encyclopedia of Chemical Technology. Interscience Publishers, a division of John Wiley and Sons, Inc. New York. 1967.

2. Fejer, M.E., and D.H. Larson. Study of Industrial Uses of Energy Relative to Environmental Effects. U.S. Environmental Protection Agency. Research Triangle Park, North Carolina. July 1974.

3. Development Document for Interim Final Effluent Limitations Guidelines and Proposed New Source Performance Standards for the Lead Segment of the Nonferrous Metals Manufacturing Point Source Category. Environmental Protection Agency. EPA-440/1-75/032-a. February 1975.

4. PEDCo-Environmental Specialists, Inc. Trace Pollutant Emissions from the Processing of Metallic Ores. August 1974.

5. Background Information for New Source Performance Standards: Primary Copper, Zinc, and Lead Smelters. Volume I, Proposed Standards. Environmental Protection Agency. Research Triangle Park, North Carolina. EPA-450/2-74-002a. October 1974.

6. Arthur G. McKee & Co. Systems Study for Control of Emissions Primary Nonferrous Smelting Industry. U.S. Department of Health, Education, and Welfare. June 1969.

7. Jones, H.R. Pollution Control in the Nonferrous Metals Industry. Noyes Data Corporation. Park Ridge, New Jersey. 1972.

Dross Reverberatory Furnace

1. Function - Dross removed from the lead bullion requires further treatment for separation of components. As cited in Process No. 7, the dross is composed of about 90 percent lead oxide, 2 percent copper, 2 percent antimony, and small amounts of other elements. Prior to smelting, the dross may be treated with soda ash, litharge or baghouse fumes, coke, and sulfur to produce matte and speiss containing high ratios of copper to lead. Whether treated or not, the dross is charged into a reverberatory furnace along with pig iron and silica. Lime rock may also be used.

During smelting, the charge separates into four layers: slag on top, matte and speiss intermediate, and molten lead at the bottom. Through the use of suitably placed taps on the furnace, each layer can be removed separately. The slag, amounting to 2 to 4 weight percent of the dross charge, is returned to the blast furnace for smelting. The slag typically assays 6 percent copper, 38 percent lead, 11 percent zinc, 11 percent FeO, and 16 percent SiO_2 (1). The matte and speiss are tapped separately, granulated, and shipped to copper smelters for recovery of copper and precious metals. The matte amounts to 10 to 14 weight percent of the dross charged; the speiss, 20 to 30 percent. The collective assay of these materials is 42 percent copper, 38 percent lead, 16 percent sulfur, 1 percent iron, and 0.6 percent arsenic, plus small amounts of zinc, rare earths, and precious metals (1). The lead layer is 94 to 98 percent lead and comprises 50 weight percent of the dross charged. It is returned to the blast furnace.

2. Input Materials - Along with the dross, the process requires the addition of pig iron, silica, and limestone. The amounts of these materials vary with each charge, depending upon dross composition. If soda treatment is used, equal amounts of soda ash, litharge, coke, and sulfur are added. Each is 3 to 5 percent by weight of the dross charged.

3. Operating Conditions - Smelting temperatures are the same as those in the blast furnace, ranging from 1000° to 1200°C. Smelting is done at atmospheric pressure.

4. Utilities - Gas or oil fuels are used for heating and maintaining temperature. Quantities are not given in the literature.

5. Waste Streams - Atmospheric emissions are the only form of pollution from the dross reverberatory furnace. Particulate emission rates are 10 kilograms per metric ton of lead produced (2). The reference does not indicate whether this emission includes condensed fume. Sulfur dioxide, carbon dioxide and monoxide, sulfur trioxide, and nitrogen and its compounds are released to the atmosphere as products of combustion. The exit gas volume from a dross reverberatory ranges from 30 to 170 normal cubic meters per minute (2,3). The SO_2 content of this gas is usually below 0.05 percent. Exhaust gases are about 760° to 980°C (2).

Water used in matte and speiss granulation is evaporated before transport.

All solids are recycled or marketed.

6. Control Technology - No control methods are used for the weak SO_2 stream emitted from the drossing reverberatory. The best available technology is chemical scrubbing.

Particulates and fumes from the drossing reverberatory are combined with the blast furnace off-gas at all plants. See Process No. 5.

7. EPA Source Classification Code - None

8. References -

1. Encyclopedia of Chemical Technology. Interscience Publishers, a division of John Wiley and Sons, Inc. New York. 1967.

2. Jones, H.R. Pollution Control in the Nonferrous Metals Industry. Noyes Data Corporation. Park Ridge, New Jersey. 1972.

3. Arthur G. McKee & Co. Systems Study for Control of Emissions Primary Nonferrous Smelting Industry. U.S. Department of Health, Education, and Welfare. June 1969.

Cadmium Recovery

1. Function - The flue dusts generated by lead smelting are processed to recover cadmium values. Since dust from blast furnace exhaust gases is recycled to the sintering machine, sinter dust becomes enriched in cadmium, thallium, and zinc. When cadmium content in the dust reaches 12 weight percent or greater, the dust is subjected to a separate roasting operation for cadmium separation and recovery (1).

Roasting is performed in one of several different types of small enclosures (2). The objective is to selectively volatilize certain of the trace elements, including cadmium, thallium, indium, and selenium and to carry these fumes out of the roaster in a stream of air. The less-volatile elements, including lead, zinc, and antimony, remain in the roaster residue which is recycled to the sintering machine feed preparation equipment.

2. Input Materials - Flue dust collected from the sintering machine exhaust gases is the only input material.

3. Operating Conditions - Operating temperature has not been reported; it is, however, carefully controlled to provide optimum separation of the trace elements.

4. Utilities - Many of these roasters are heated electrically and others are heated with oil or gas. The energy consumption of these units has not been reported.

5. Waste Streams - Fume emissions from the roaster are cooled and recovered as product. The roaster residue is recycled. Data for fume capture are not furnished in the literature.

There are no liquid or solid wastes from cadmium recovery.

6. Control Technology - The flue dust and fume emitted from the roaster can be contained by further cooling with water sprays and collection in a baghouse.

7. EPA Source Classification Code - None

8. References -

1. Arthur G. McKee & Co. Systems Study for Control of Emission Primary Nonferrous Smelting Industry. U.S. Department of Health, Education, and Welfare. June 1969.

2. Hallowell, J.B., et al. Water Pollution Control in the Primary Nonferrous Metals Industry. Volume I, Copper, Zinc, Lead Industries. Environmental Protection Agency. Washington, D.C. EPA-R2-73-274a. September 1973.

Reverberatory Softening

1. Function - The drossed lead bullion is further purified by a process termed "softening", which entails removal of the elements that make lead hard, notably arsenic, antimony, and tin. Several other softening processes can be used (Process No's. 11 and 12) (1,2).

The reverberatory method is similar to the drossing procedure and is particularly applicable to processing bullion with a wide range of impurities. The bullion is charged into a reverberatory furnace, melted, and blown with air to effect oxidation of the arsenic, antimony, tin, and other impurities. If hardness of the feed bullion is greater than 0.3 to 0.5 weight percent antimony equivalent, litharge is added to increase the rate of impurity oxidation (1).

Furnaces with capacities of up to 300 metric tons are used for the process. The oxides rise to the surface to form a slag that is skimmed off and further treated to recover contained values. The softened lead is tapped from the bottom of the furnace and pumped to the desilverizing process. Table 28 presents typical analyses of the softened bullion product and the softened slag. Hardness of the softened bullion is less than 0.03 weight percent antimony equivalent.

2. Input Materials - An analysis of drossed lead was presented in Table 27 (Process No. 7). Litharge is added only when especially hard bullion is processed. Coke or coal may be added to inhibit the oxidation of lead.

3. Operating Conditions - Temperatures during softening reach 700°C. Pressures are atmospheric (1).

4. Utilities - Electricity is the power source for mechanical agitators, pumps, and conveyors. Most of the heat is supplied by the exothermic oxidation of impurities. Any fossil fuel can be used to begin the reaction and maintain the temperature. Air is injected through lances or pipes into the bath. Air consumption is not reported.

5. Waste Streams - The air blow from the furnace is the only waste stream for the process. No data are reported for fume emissions.

There are no liquid or solid wastes from reverberatory softening.

6. Control Technology - No controls of atmospheric fume emissions are reported. The exhaust gas could be routed to blast furnace baghouses.

7. EPA Source Classification Code - None

TABLE 28. TYPICAL COMPOSITIONS OF SOFTENED LEAD BULLION AND SLAG (1)
(AMOUNTS IN WEIGHT PERCENT)

Constituent	Softened lead bullion	Softened slag (liquid dross)
Pb		75.
Cu	0.004	0.005
Se		tr
Te		tr
As	0.001	1.7
Sb	0.025	12.0
Sn		tr
Ag	0.15	tr
Au	1.25[a]	tr

[a] Value for gold in grams per metric ton.

tr - trace.

8. References -

1. Encyclopedia of Chemical Technology. Interscience Publishers, a division of John Wiley and Sons, Inc. New York. 1967.

2. Development Document for Interim Final Effluent Limitations Guidelines and Proposed New Source Performance Standards for the Lead Segment of the Nonferrous Metals Manufacturing Point Source Category. Environmental Protection Agency. EPA-440/1-75/032-a. February 1975.

Kettle Softening

1. Function - Arsenic, antimony, and tin may be removed from the drossed lead bullion by kettle softening. Other softening methods are reverberatory (Process No. 10) and Harris (Process No. 12). Unlike the reverberatory method, in which air is blown through molten bullion, the kettle method entails addition of oxidizing agents to remove impurities. Application is usually limited to treating bullion with a relatively low impurity content, 0.3 weight percent or less antimony equivalent (1,2).

Drossed bullion is charged to a kettle and melted. Oxidizing fluxes such as caustic soda (NaOH) and niter ($NaNO_3$) are then added while the charge is agitated. The fluxes react with the impurities to form a series of salts such as sodium antimonate ($NaSbO_3$) (1,3). A slag containing the oxidized impurities results. When the reactions are complete, agitation of the kettle is stopped, and the slag rises to the top of the kettle, where it is skimmed off; the purified lead bullion is sent to the desilvering process. Composition of the softened bullion is similar to that shown in Table 28 (Process No. 10); residual hardness is less than 0.03 weight percent antimony equivalent.

2. Input Materials - In addition to the drossed lead bullion, caustic soda and sodium nitrate (niter) are required for fluxing. Amounts depend upon the impurity content of the feed bullion; a slight excess over stoichiometric requirements is desirable for effective removal of impurities.

3. Operating Conditions - A kettle temperature of 700°C is required. Pressure is atmospheric (1).

4. Utilities - Electricity is used to power the process equipment, such as agitators and conveyors. Gas or oil are used to heat the kettle and maintain temperature.

5. Waste Streams - Atmospheric emissions containing oxides of nitrogen are released during kettle softening. Details are unreported.

There are no liquid wastes from this process.

The slag containing oxidized impurities is discarded. This material contains lead as well as water-soluble sodium oxide salts of arsenic, tin, and antimony. The amount of slag generated is not reported.

6. Control Technology - The controls used for atmospheric emissions are not known.

Slag is dumped with that generated in either the blast furnace or fuming furnace (2). There is no recognized control technology for disposition of this slag. Substitution of Harris softening (Process No. 12) is recommended.

7. EPA Source Classification Code - None

8. References -

1. Encyclopedia of Chemical Technology. Interscience Publishers, a division of John Wiley and Sons, Inc. New York. 1967.

2. Hallowell, J.B., et al. Water Pollution Control in the Primary Nonferrous Metals Industry - Volume I. Copper, Zinc, and Lead Industries. Environmental Protection Agency. Washington, D.C. EPA-R2-73-274a. September 1973.

3. Development Document for Interim Final Effluent Limitations Guidelines and Proposed New Source Performance Standards for the Lead Segment of the Nonferrous Metals Manufacturing Point Source Category. Environmental Protection Agency. EPA-440/1-75/032-a. February 1975.

Harris Softening

1. Function - In addition to reverberatory and kettle softening, removal of arsenic, antimony, and tin from drossed lead bullion can also be accomplished by the Harris process. As with kettle softening, the process is most applicable in treating bullions containing 0.3 percent or less antimony.

The process consists of two operations. The initial pyrometallurgical step is the same as the kettle softening process. The drossed bullion is charged to a kettle, melted, and agitated. Sodium nitrate and sodium hydroxide are added to react with the impurities and form metallic salts which float on top of the bath in a mixture with sodium oxide. These salts are skimmed off, and the purified lead is sent to the desilverizing process (1).

The second operation is a hydrometallurgical treatment of the cooled skimmings, in which hot water is used to dissolve the valuable constituents. Most of the skimmings will be dissolved and will form a strongly alkaline solution. Any undissolved residue is filtered from the mixture and discarded. The clear solution is then cooled to preferentially precipitate sodium antimonate. After separation by filtration, the antimony-rich filter cake is subjected to further processing (Process No. 13), and the filtrate is mixed with lime to precipitate calcium salts of arsenic and tin in separate operations.

Upon removal from solution, the calcium arsenate is reported to be sold to insecticide manufacturers, and the calcium stannate is shipped to tin producers. The residual sodium hydroxide solution is evaporated to produce dry sodium hydroxide, which is recycled to the softening process.

2. Input Materials - Aside from the drossed lead bullion, sodium hydroxide and sodium nitrate are required in slightly more than stoichiometric amounts for fluxing. Unspecified amounts of process water are fed to the operation for leaching. Lime is required in quantities sufficient to precipitate salts of arsenic and tin.

Use of sodium chloride and lead oxide in this process has also been reported.

3. Operating Conditions - Maximum temperatures are 700°C for the pyrometallurgical operation, 100°C for hydrometallurgical processing, and more than 200°C for sodium hydroxide evaporation (2). Atmospheric pressure is maintained during all operations.

4. Utilities - Process equipment, such as agitators, pumps, and conveyors, are powered by electricity.

Gas or oil is utilized for kettle heating, temperature maintenance, and sodium hydroxide recovery.

5. Waste Streams - Atmospheric emissions containing oxides of nitrogen will result from the use of sodium nitrate as an input material.

The quantity of insoluble residue created from the leaching step has not been reported. Its composition is also unknown, but it has been reported to be insoluble in water (1).

6. Control Technology - No control of air emissions from this process is employed. The leaching residue is apparently discarded along with blast furnace or fuming furnace slag.

7. EPA Source Classification Code - None

8. References -

1. Hallowell, J.B. et al. Water Pollution Control in the Primary Nonferrous Metals Industry - Volume I. Copper, Zinc, and Lead Industries. Environmental Protection Agency. Washington, D.C. EPA-R2-73-274a. September 1973.

2. Encyclopedia of Chemical Technology. Interscience Publishers, a division of John Wiley and Sons, Inc. New York. 1967.

Antimony Recovery

1. Function - Slags from the softening processes (Process No's. 10, 11, 12) are treated in order to separate and recover the contained mineral values, notably arsenic, tin, and antimony. Two methods are commonly used to recover antimony, depending upon the product desired.

If antimonial lead or "hard lead" is desired, the softening slag is subjected to a reduction process. The slag is charged to a furnace and heated with a reducing agent and slagging fluxes. Since the oxidation potential of the other minerals in the charge is higher, the oxides of lead and antimony are preferentially reduced. Slag is formed and skimmed off while the metallic mixture of lead and antimony is tapped as a marketable product. If the slag is rich in tin, it may be sold to a tin producer; otherwise, it is recycled to the sintering process or blast furnace (1).

If the desired product is antimony trioxide (Sb_2O_3), the softening slag feed is treated by a volatilization process. The slag is fed to a furnace, where it is heated to volatilize arsenic trioxide and antimony trioxide. Since arsenic trioxide is more volatile, it is driven off first and is separated from the antimony tricxide by selective condensation (2). Collection of the oxides consists of condensing the volatilized fume and capturing it in an electrostatic precipitator or a baghouse. The recovered antimony trioxide is sent to antimony refining plants, usually located nearby. Recovered arsenic trioxide may be sold to arsenic processors. The nonvolatilized furnace residue, containing appreciable lead values, is returned to the blast furnace or sintering process.

2. Input Materials - Slag from the softening processes is the main input; it contains primarily lead, arsenic, antimony, and tin. A typical analysis is presented in Table 28 (Process No. 10). For production of hard lead, coke or charcoal is used as a reductant, the quantity dependent on feed slag composition. Soda ash or silica is used as a flux. No quantitative data are reported.

3. Operating Conditions - Temperatures range from 800° to 900°C. Pressures are atmospheric (2).

4. Utilities - Gas or oil is used to maintain furnace temperatures. Electricity is required for operation of conveyors. In antimony trioxide production, cooling water is required for fume condensation. No quantitative data are furnished in the literature.

5. Waste Streams - In the volatilization process, the airstream carrying the oxide fume is released to the atmosphere after condensation and collection.

There are no liquid wastes from antimony recovery.

The arsenic trioxide, if it cannot be sold, represents the only solid waste from the process.

6. Control Technology - In the volatilization and condensation process, the fume stream passes through an electrostatic precipitator or baghouse (3).

No established control for excess arsenic trioxide has been developed.

7. EPA Source Classification Code - None

8. References -

1. Hallowell, J.B., et al. Water Pollution Control in the Primary Nonferrous Metals Industry. Volume I, Copper, Zinc, and Lead Industries. Environmental Protection Agency. Washington, D.C. EPA-R2-72-274a. September 1973.

2. Encyclopedia of Chemical Technology. Interscience Publishers, a division of John Wiley and Sons, Inc. New York. 1967.

3. Development Document for Interim Final Effluent Limitations Guidelines and Proposed New Source Performance Standards for the Lead Segment of the Nonferrous Metals Manufacturing Point Source Category. Environmental Protection Agency. EPA-440/1-75/032-a. February 1975.

Parkes Desilverizing

1. Function - Gold and silver are removed from the softened lead bullion by the Parkes desilverizing process. These metals do not oxidize easily, and they are not removed by any of the previous refining steps. The Parkes desilverizing process is based on the fact that gold and silver have a greater affinity for zinc than for lead. Therefore, zinc is added to the molten lead bullion to form alloys with the copper, gold, and silver contained in the bullion. These alloys are insoluble in the lead and rise to the surface, forming a crust that is skimmed off.

To simplify subsequent recovery processes, the gold and silver are often recovered in separate steps. Since gold and most of the copper are first to combine, zinc is added in two steps. The initial addition results in a crust rich in gold values (1,2). Following removal of this crust, the second addition of zinc is made to allow the removal of silver. Although these steps are not totally exclusive for either gold or silver, they do effect a good degree of segregation.

Because other metallic impurities, notably arsenic, can interfere with this process, they must be removed prior to this operation. Arsenic content in the bullion must be less than 0.10 weight percent (1).

2. Input Materials - Softened lead bullion is required for the process. Hardness equivalent to less than 0.03 combined weight percent of arsenic, antimony, and tin is desirable. A typical analysis for a softened bullion is presented in Table 28, Process No. 10.

Zinc is the only additive. The amount is 1 to 2 percent in excess of the amount required to saturate the lead bullion, i.e., 0.55 weight percent of bullion weight.

3. Operating Conditions - The bullion charge is heated to 540°C and then cooled to 40° to 93°C (1,3). Pressure is atmospheric.

4. Utilities - Gas or oil is used to heat the charge. Electricity is used to operate pumps and agitators. Utility quantities are not given in the literature.

5. Waste Streams - None

6. Control Technology - None

7. EPA Source Classification Code - None

8. References -

1. Encyclopedia of Chemical Technology. Interscience Publishers, a division of John Wiley and Sons, Inc. New York. 1967.

2. Hallowell, J.B., et al. Water Pollution Control in the Primary Nonferrous Metals Industry. Volume I, Copper, Zinc, and Lead Industries. Environmental Protection Agency. Washington, D.C. EPA-R2-73-274a. September 1973.

3. Development Document for Interim Final Effluent Limitations Guidelines and Proposed New Source Performance Standards for the Lead Segment of the Nonferrous Metals Manufacturing Point Source Category. Environmental Protection Agency. EPA-440/1-75/032-a. February 1975.

Retorting

1. Function - Crusts from the Parkes process are retorted to recover zinc for reuse in the desilvering process and to form a purified Doré metal. Dross is placed in graphite crucibles of 600 to 640 kilograms capacity; these are heated in a special Faber-du-Faur-type furnace, and the zinc is vaporized. The zinc vapor is condensed in a cooling chamber and then tapped to bars or blocks for recycle. The remaining retort metal assays 140 to 400 kilograms Doré per metric ton of dross (1). Table 29 presents a typical analysis of this retort metal.

TABLE 29. TYPICAL RETORT ANALYSIS (1)

Constituent	% weight	Constituent	% weight
Doré	15.6-43.8	Copper	1.5-4.0
Zinc	1.5-2.5	Tellurium	0.2
Arsenic	0.4	Bismuth	0.25
Antimony	1.0	Lead	Remaining percentage

2. Input Materials - Crusts from the desilverizing process are the only input materials for this process. This dross is basically a gold-silver-zinc compound with small amounts of impurities such as antimony, copper, tellurium, bismuth, and lead.

3. Operating Conditions - Operating temperatures during retorting are between 1260° and 1320°C (1). Pressure is atmospheric.

4. Utilities - The retort furnaces are gas- or oil-fired. Electricity is consumed by transport apparatus. No quantities are cited.

5. Waste Streams - The only waste stream consists of small quantities of metallic fume escaping the condensing chamber. This fume is believed to be composed predominately of zinc, arsenic, antimony, and lead. No data were found on emission factors or constituents.

6. Control Technology - Several smelters control fume and particulate emissions with baghouses. Destruction of baghouse fabric at high temperatures is prevented by routing the gases through tubular cooling chambers prior to entering the baghouse. Control efficiencies of more than 98 percent are claimed. The collected flue dusts are recycled to the sintering machine. Other smelters use no control devices on retorts.

7. EPA Source Classification Code - None

8. References -

1. Encyclopedia of Chemical Technology. Interscience Publishers, a division of John Wiley and Sons, Inc. New York. 1967.

Cupelling

1. Function - Retort metal is purified in the process called cupelling. In a furnace called a cupel, the molten metal charge is successively blown with air and slagged to remove impurities and produce a relatively pure Doré. The difference in oxidation potentials of the impurities allows sequential removal of slags with distinct characteristics.

Zinc, arsenic, and antimony are oxidized first and removed; most of the lead content oxidizes next, forming a product called "good litharge." Upon removal, it is recycled to the softening process for use as an oxidizer. Bismuth, copper, and tellurium accumulate in the Doré until the final stages of cupelling, when they oxidize to a slag called "coppery litharge" because the copper content may be as high as 10 weight percent. Oxidizing agents are required to remove the last traces of copper and tellurium from the Doré. These latter slags are returned to smelting for further processing.

Cupels are rated according to Doré output. Usual capacities range from 2,850 to 11,300 kilograms per charge. When impurity removal is complete, the remaining gold-silver alloy is cast into bars for marketing. Purity is 99.9 percent.

2. Input Materials - Retort metal is the basic feed to the process. A typical analysis of the metal is given in Table 29, Process No. 15.

Sodium nitrate and silica flour are added to remove the last traces of copper and tellurium from the Doré. Amounts depend upon residual levels of the impurities.

3. Operating Conditions - Temperature of the cupel reaches 1150°C (1). Pressure is atmospheric.

4. Utilities - Gas or oil is used to heat the furnace. Pumps and agitators are electrically powered. Cooling water is pumped through jacketed furnace sections. Compressed air is injected into the charge for oxidation of impurities. A cold air stream is also blown across the face of the bath at a pressure of 70 to 87 grams per square centimeter to cause rippling, which hastens oxidation. No additional quantitative data are given.

5. Waste Streams - Process exhaust gases range in temperature from 1000° to 1100°C and contain metallic vapors (fume) as well as particulates. Zinc, lead, arsenic, and antimony comprise the fume. Particulates may contain any of the components listed in Table 29 (Process No. 15). Emission data are not present in the literature.

6. Control Technology - Several smelters control exhaust gases, cooling them by passage through tubular cooling chambers before routing them to baghouses. Collection efficiency greater than 98 weight percent is claimed. Collected dust is recycled to the smelter for further processing. Other smelters do not control cupel emissions.

7. EPA Source Classification Code - None

8. References -

1. Encyclopedia of Chemical Technology. Interscience Publishers, a division of John Wiley and Sons, Inc. New York. 1967.

Vacuum Dezincing

1. Function - Zinc added to the bullion in the desilverizing process is removed by dezincing. The vacuum distillation method is used most widely in the industry because the recovered metallic zinc can be directly recycled to the desilvering process. Alternate methods are chlorine dezincing (Process No. 18) and Harris dezincing (Process No. 19).

Desilverized lead is charged into a kettle and heated. An inverted bell is placed on top of the kettle with its skirt projecting into the molten lead to form a vacuum seal. A vacuum is drawn in the bell and is held for about 2.5 hours, during which the bath is agitated to bring the zinc to the surface. The zinc vaporizes and is condensed on the water-cooled dome of the bell. On completion of the process, the vacuum is broken, the bell removed, and the solidified zinc peeled from the surface of the bell.

The product bullion typically is analyzed as less than 0.001 weight percent zinc, 0.0003 weight percent antimony, and 0.15 weight percent bismuth (1). The bullion is sent for debismuthizing or for casting if bismuth content is low (2).

2. Input Materials - Desilverized lead bullion typically containing 0.5 to 1.0 weight percent zinc is the only feed material (3).

3. Operating Conditions - The molten lead bath is maintained at 580° to 595°C (1,2) with an operating pressure of 50 to 60 micrometers absolute (1).

4. Utilities - Gas or oil is used to maintain the kettle temperature. Pumps, agitators, and conveyors are electrically powered. Cooling water is used to remove heat from the jacketed bell surface. Although no quantitative data are given in the literature, energy consumption is higher than in other dezincing processes because of the higher temperature requirements.

5. Waste Streams - None

6. Control Technology - None

7. EPA Source Classification Code - None

8. References -

1. Encyclopedia of Chemical Technology. Interscience Publishers, a division of John Wiley and Sons, Inc. New York. 1967.

2. Hallowell, J.B., et al. Water Pollution Control in the Primary Nonferrous Metals Industry. Volume I, Copper, Zinc, and Lead Industries. Environmental Protection Agency. Washington, D.C. EPA-R2-73-274a. September 1973.

3. Development Document for Interim Final Effluent Limitations Guidelines and Proposed New Source Performance Standards for the Lead Segment of the Nonferrous Metals Manufacturing Point Source Category. Environmental Protection Agency. EPA-440/175-032a. February 1975.

Chlorine Dezincing

1. Function - Desilverized lead bullion requires removal of the zinc added during the desilverizing process. A process known as chlorine dezincing, or the Betterton process, can be used, as well as vacuum dezincing (Process No. 17) and Harris dezincing (Process No. 19).

Molten lead is pumped from a heated kettle to a reaction chamber into which gaseous chlorine is injected from a chlorine tank. Since reactivity of zinc with chlorine is greater than that of lead, zinc chloride is formed in the reactor and subsequently collects on the surface of the molten lead. The material skimmed from the lead contains small amounts of lead chloride and mechanically entrained lead prills. After treatment with metallic zinc for lead removal and recovery, a marketable byproduct analyzed as 99 percent zinc chloride is obtained. The dezinced lead bullion is sent for debismuthizing or casting.

A 180-metric-ton kettle with an overall cycle of about 8 hours typically produces 16,300 metric tons of dezinced bullion per month. The bullion contains 0.005 weight percent zinc (1).

2. Input Materials - The desilverized lead bullion feed contains 0.5 to 1.0 weight percent zinc.

Chlorine is injected at a rate of 180 to 225 kilograms per hour into molten lead recirculated at a rate of 7 to 11 metric tons per minute (1).

3. Operating Conditions - A temperature of 370°C maintains the lead in a molten condition. Pressure is atmospheric (1).

4. Utilities - The kettle is heated with oil or gas. Electricity is used for pumps, agitators, and conveyors. No quantitative data regarding consumption are cited.

5. Waste Streams - None

6. Control Technology - None

7. EPA Source Classification Code - None

8. References -

1. Encyclopedia of Chemical Technology. Interscience Publishers, a division of John Wiley and Sons, Inc. New York. 1967.

Harris Dezincing

1. Function - Zinc added to the lead bullion for desilverizing requires removal by a dezincing process. The Harris dezincing process consists of a pyrometallurgical step followed by a hydrometallurgical procedure. Alternate dezincing processes are vacuum (Process No. 17) and chlorine (Process No. 18).

The pyrometallurgical equipment is the same as for Harris softening (Process No. 12), i.e., a charging kettle, a reaction cylinder, and a molten lead pump. In a typical cycle, desilverized lead bullion is charged to the kettle and then pumped, in a molten state, through the reaction cylinder, which contains a small amount of caustic soda saturated with lead oxide. The saturated caustic remains from the previous dezincing cycle. Upon contact with the molten lead, the lead oxide in the caustic reacts with the zinc to form zinc oxide, which in turn reacts with caustic to form sodium zincate. After 30 minutes of lead recirculation, pumping is stopped, fresh caustic is added to the cylinder to maintain salt fluidity, and the contents of the cylinder are emptied into a granulator tank. Fresh molten caustic is again pumped to the cylinder, and recirculation of the lead bullion is resumed. The final caustic addition will become saturated with zinc and lead oxide and is held over for the next cycle. When dezincing is complete, the product contains less than 0.001 weight percent zinc and 0.0003 weight percent antimony. The dezinced lead is pumped from the kettle for debismuthizing or casting.

The spent salts from the granulation tank are treated hydrometallurgically. After granulation and solution in hot water, sodium zincate hydrolyzes to zinc oxide and sodium hydroxide. The zinc oxide precipitates from the solution and is recovered by filtration. It is subsequently dried and sold. The sodium hydroxide solution is evaporated, and the resulting anhydrous caustic recycled (1).

2. Input Materials - Desilverized lead containing 0.5 to 1.0 weight percent lead is charged to the process. Anhydrous sodium hydroxide is required, the amount dependent upon the zinc content of the feed bullion. Water is used for the hydroextraction of byproducts. No data as to quantities are given.

3. Operating Conditions - A temperature of 540°C is required for the pyrometallurgical operation. The temperature for hydroextraction is 100°C. Evaporation of the sodium hydroxide solution requires temperatures above 200°C. All operations are performed at atmospheric pressure (1).

4. Utilities - Kettle heating and soda evaporation of caustic require gas or oil as fuel. Electricity is used to operate pumps, agitators, and conveyors.

5. Waste Streams - None

6. Control Technology - None

7. EPA Source Classification Code - None

8. References -

1. Encylopedia of Chemical Technology. Interscience Publishers, a division of John Wiley and Sons, Inc. New York. 1967.

Debismuthizing

1. Function - When the dezinced lead bullion contains 0.15 weight percent or more bismuth, it must be debismuthized before the final refining and casting process. The debismuthizing procedure is called the Betterton-Kroll process.

Calcium and magnesium are added to the molten lead to form ternary compounds (e.g., $CaMg_2Bi_2$) with the bismuth (1). The compounds have a higher melting point than lead and a lower density. Therefore, when the temperature of the mixture is reduced to just above the melting point of lead, the metallic compounds solidify to form a dross that can be skimmed from the lead. To enhance physical separation, antimony or organic agents are sometimes added. Chlorine steam may also be used.

The purified lead is pumped to the casting operation, and the skimmed metallic compound is sent to bismuth recovery.

Cupel slags rich in bismuth may be similarly treated; the residual lead is returned to smelting.

2. Input Materials - Dezinced lead bullion fed to the process typically assays 0.001 weight percent zinc, 0.0003 weight percent antimony, and 0.15 weight percent bismuth (2). The quantities of calcium and magnesium added depend on the amount of bismuth to be removed. Twice as much calcium is added as magnesium. Cupel slags are added when bismuth content is high enough (20 to 25 weight percent) to warrant recovery. Antimony or organic compounds are added as needed to improve bismuth separation. The literature does not specify the organic compounds or the amounts.

3. Operating Conditions - The molten lead bath is maintained at 500° to 550°C (1,3) for calcium-magnesium addition and is cooled to 350°C for dross separation. Pressure is atmospheric.

4. Utilities - A small amount of gas or oil is required to maintain the lead bath temperature. Pumps and agitators are electrically powered.

5. Waste Streams - None

6. Control Technology - None

7. EPA Source Classification Code - None

8. References -

1. Development Document for Interim Final Effluent Limitations Guidelines and Proposed New Source Performance Standards for the Lead Segment of the Nonferrous Metals Manufacturing Point Source Category. Environmental Protection Agency. EPA-440/1-75/032-a. February 1975.

2. Encyclopedia of Chemical Technology. Interscience Publishers, a division of John Wiley and Sons, Inc. New York. 1967.

3. Hallowell, J.B., et al. Water Pollution Control in the Primary Nonferrous Metals Industry. Volume I, Copper, Zinc, and Lead Industries. Environmental Protection Agency. Washington, D.C. EPA-R2-73-274a. September 1973.

Bismuth Refining

1. Function - The dross generated by debismuthizing is processed for bismuth recovery. The material is placed in a furnace, where it is melted. Chlorine gas is injected, and the calcium, magnesium, zinc, and lead combine with the chlorine to form chlorides more readily than does bismuth. The chlorides form a solid slag that is skimmed from the surface of the molten bismuth. Air is then blown through the bismuth, and a caustic soda flux is added to oxidize any residual impurities. After slag removal, the metal, which is now 99.99 percent bismuth, is cast into marketable shapes and sold (1).

Alternate methods of bismuth refining are also in use involving wet chemical processing; these methods are not addressed in this report.

2. Input Materials - The slag from the debismuthizing process is chiefly composed of ternary compounds of calcium, magnesium, and bismuth. Chlorine constitutes about 25 weight percent of the slag charged to the furnace. Caustic soda flux is used in varying amounts for oxidation of impurities. Charcoal is used as a cover during casting to maintain the bismuth in a reduced state.

3. Operating Conditions - Bath temperature during chlorination is 500°C. Subsequent temperatures for oxidation and casting are lower. Pressure is atmospheric (1).

4. Utilities - Gas or oil is used for heating and maintaining temperature. Electricity is used to run pumps and agitators. Compressed air is furnished to oxidize impurities. The literature does not state the quantities required.

5. Waste Streams - Exhaust gases to the atmosphere contain chlorine and fume. No emission quantities were found.

There are no liquid wastes from the process.

Slag composed of chlorides of calcium, magnesium, zinc, and lead is 40 weight percent of the dross fed to the process. Final oxidation generates a soda slag in unspecified amounts.

6. Control Technology - Control of atmospheric emissions is not practiced.

Slags are discarded with those generated in smelting. Further information is given in Process No's. 5 and 6. The chloride salts contained in the slag are very water-soluble and easily leached into adjacent water supplies. Existing practice does not represent good control technology.

7. EPA Source Classification Code - None

8. References -

1. Encyclopedia of Chemical Technology. Interscience Publishers, a division of John Wiley and Sons, Inc. New York. 1967.

Final Refining and Casting

1. Function - Refined lead bullion from dezincing or debismuthizing is given a final purification and cast into ingots. The refined lead is fluxed with oxidizing agents to remove remaining impurities such as lead oxide and magnesium or calcium residues. After slag removal by skimming, the lead, assayed as 99.999 percent purity, is reheated and sent to the casting operation, where it is formed into ingots or pigs. Most casting is performed by fully automated machines. Slag is recycled to the blast furnace (1).

2. Input Materials - Refined bullion containing a small amount of impurities is fed to the process. Caustic soda and sodium nitrate are used as oxidizing flux in amounts varying with the impurity of the lead (1,2). Water is used to cool the cast lead ingots by direct contact, at rates ranging from 300 to 1,500 liters per minute (3).

3. Operating Conditions - Temperatures for final purification range from 370° to 500°C; casting is at 540°C (1,4). Pressure is atmospheric.

4. Utilities - Gas or oil is required for heating. Pumps and agitators are electrically operated. The literature gives no data on quantities.

5. Waste Streams - Small amounts of atmospheric emissions are released during refining and casting operations. Emission factors and constituents have not been reported.

Direct-contact cooling water becomes contaminated with particulate matter, including lead and lead oxides.

6. Control Technology - There are no controls on the atmospheric emissions.

Several methods are used to handle the contaminated cooling water. The water is either recycled for use in slag granulation or is sent to a tailings pond for settling of suspended solids. A variation of the latter method, liming the effluent for precipitation of solids, is also practiced (3).

7. EPA Source Classification Code - None

8. References -

1. Encyclopedia of Chemical Technology. Interscience Publishers, a division of John Wiley and Sons, Inc. New York. 1967.

2. Development Document for Interim Final Effluent Limitations Guidelines and Proposed New Source Performance Standards for the Lead Segment of the Nonferrous Metals Manufacturing Point Source Category. Environmental Protection Agency. EPA-440/1-75/032-a. February 1975.